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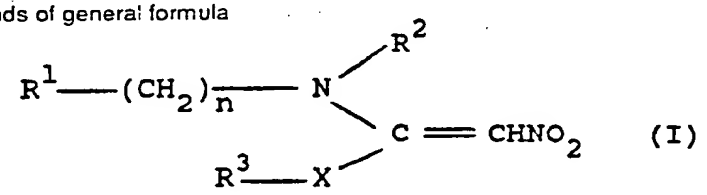
(54) Pesticidal nitroethene compounds

(57) Nitroethene compounds of general formula



(I)

wherein n is 0 or 1, X represents a sulphur atom or a group N-R^4, R^1 represents an optionally substituted pyridyl group, R^2 represents a hydrogen atom or a C_{1-6} alkyl group, R^3 represents a methyl or ethyl group and R^4 represents a hydrogen atom or a methyl or ethyl group, have pesticidal, particularly insecticidal, activity and can be incorporated into pesticidal compositions.

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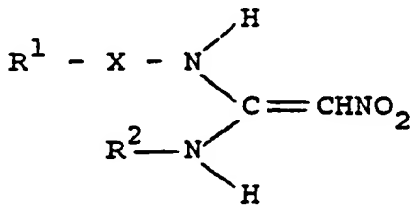
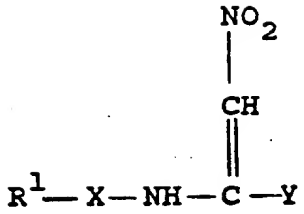
NITROETHENE COMPOUNDS, THEIR PREPARATION AND THEIR USE AS PESTICIDES

This invention relates to nitroethene compounds, to processes for their preparation, and to the use of such compounds as pesticides.

US Patent No. 4,567,188 (and the corresponding EP-A-104423) discloses 2-nitro-1,1- ethenediamines of formula



in which R^1 represents an aryl or heteroaryl radical, which is optionally substituted, R^2 represents straight chain, branched or cyclic alkyl or alkenyl, which is optionally substituted by alkoxy or cycloalkyl, or an optionally substituted aryl or heteroaryl radical and X represents a single bond or a methylene group, which is optionally alkyl-substituted, and R^2 is not aryl if X represents a single bond, and their physiologically acceptable acid addition salts and their isomeric forms, in particular the cis-and trans-isomers.
Also disclosed are 2-nitro-1-aminoethenes of formula



in which R^1 and X are as defined above and Y is, inter alia, alkylmercapto, and their reaction with amines of formula R^2-NH_2 to produce the above 2-nitro-1,1-ethenediamines.

The 2-nitro-1,1-ethenediamines are disclosed as having pharmacological activity rendering them suitable for pharmaceutical application in the prophylaxis of acute and chronic ischaemic heart disease in the broadest sense, for the therapy of high blood pressure and for the treatment of disorders in cerebral and peripheral blood flow.

It is specifically stated in both US Patent No. 4,567,188 and EP-A-104423 that in definition of R^2 in the above general formulae alkyl preferably represents straight-chain or branched alkyl with 1 to 10, in particular 3 to 8, carbon atoms.

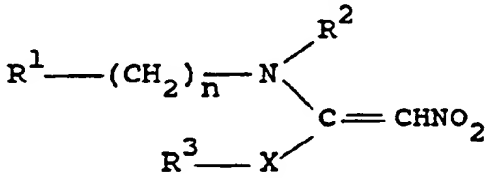
In the 2-nitro-1,1-ethenediamines specifically exemplified in US Patent No. 4,567,188 and EP-A-104423, R^1 is variously phenyl, 2,6-dimethylphenyl, 2,4,6-trimethylphenyl, 2,3-dimethylphenyl, 4-chloro-2-methylphenyl, 3-chloro-4-methylmercaptophenyl, 3-chloro-4-methoxyphenyl, 2-ethoxyphenyl, 2-methoxyphenyl, 4-hydroxyphenyl, 2,4-dimethoxyphenyl, 4-ethoxyphenyl, 3-methoxyphenyl, 3-ethoxyphenyl, 2-pyridyl, 3-pyridyl or 4-pyridyl. R^2 is variously phenyl, 4-ethoxyphenyl, 2,3-dimethylphenyl, 2,6-dimethylphenyl, 4-methoxyphenyl, 3,4-dimethoxyphenyl, 3-chloro-4-methoxyphenyl, cyclohexyl, 1,2,2-trimethylpropyl, n-hexyl, 2-methoxyethyl, 1,1-dimethylethyl, 2,2-dimethylpropyl or

2-ethylbutyl.

It is of particular note that in the exemplified compounds of US Patent No. 4,567,188 or EP-A-104423 where R^2 is an unsubstituted alkyl group, in no case does the alkyl group contain fewer than 4 carbon atoms.

There has now surprisingly been discovered a special class of nitroethene compounds which exhibit pesticidal, particularly insecticidal, activity.

According to the present invention there are provided nitroethene compounds of general formula



(I)

wherein n is 0 or 1, X represents a sulphur atom or a group N-R^4, R^1 represents an optionally substituted pyridyl group, R^2 represents a hydrogen atom or a C_{1-6} alkyl group, R^3 represents a methyl or ethyl group and R^4 represents a hydrogen atom or a methyl or ethyl group.

R^1 is preferably an optionally substituted 3-pyridyl group. Examples of optional substituents on a pyridyl group include halogen atoms and alkyl, alkoxy, alkylthio, haloalkyl, cyano, alkoxycarbonyl, alkylamino, dialkylamino, (alkylcarbonyl)alkylamino, (alkoxycarbonyl)alkylamino, alkylcarbonylamino, and alkoxycarbonylamino groups. Any alkyl moiety in such substituents is preferably C_{1-6} alkyl, more preferably C_{1-4} alkyl.

Preferred compounds of formula I have one or more of the following features:-

(i) R^1 is a 3-pyridyl group substituted in the 6-position by a halogen atom, a C_{1-4} alkoxy group, a C_{1-4} alkylthio group, a

C_{1-4} haloalkyl group, a cyano group or a (C_{1-4} alkoxy)carbonyl group,

(ii) R^1 is a 3-pyridyl group substituted in the 6-position by a chlorine or bromine atom, a methoxy group, a di- or trifluoromethyl group, or a cyano group,

(iii) R^1 is a 6-chloro-3-pyridyl group,

(iv) R^2 is a hydrogen atom or a C_{1-4} alkyl group,

(vi) X is N-R^4,

(vii) X is N-R^4, R^3 is a methyl group and R^4 is a hydrogen atom or a methyl group, and

(viii) n is 1.

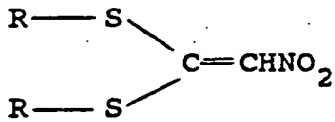
Preferred combinations of the above features include (i), (vi) and (viii); (ii), (vi) and (viii); (iii), (vi) and (viii); (iii), (vii) and (viii), and any of the preceding combinations together with (iv) or (v).

Those skilled in the art will appreciate the possibility of the compounds of formula I existing as isomers (cis- and trans-isomers) and as tautomers. All such isomers and tautomers and their mixtures are embraced by the present invention, as also are the compounds of formula I in the form of their acid-addition salts.

The invention further provides a process for the preparation of a compound of general formula I as defined above which comprises reacting a compound of formula

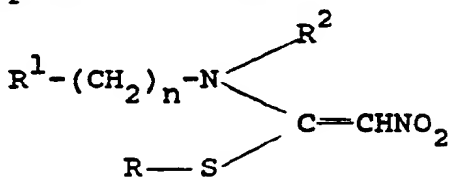
$$R^1-(CH_2)_n-NH-R^2 \qquad (II)$$

wherein n, R^1 and R^2 are as defined above with a nitroethene compound of formula



(III)

wherein R represents a C_{1-4} alkyl group, to produce a nitroethene compound of formula



(IV)

followed, optionally where R is R^3, by reacting the compound of formula IV with an amine of formula R^3R^4NH wherein R^3 and R^4 are as defined above, to produce a compound of formula I wherein X is $N-R^4$.

The compounds of formula III are known and are described in DE-A-2514402. 1,1-bismethylthio-2-nitroethene is specifically described by Gompper and Schaeffer, Chem, Ber., 100, 591-604 (1967).

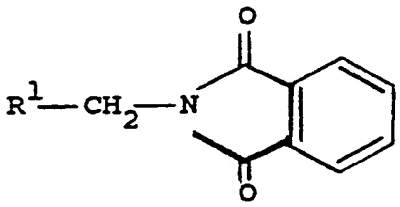
Reaction of the compound of formula II with the compound of formula III may conveniently be effected in the presence of an inert solvent such as alcohols, conveniently ethanol, or other polar solvents such as dimethylformamide, dimethylacetamide, N-methylpyrrolidone, dimethylsulphoxide or acetonitrile. The reaction may conveniently be effected at a temperature in the range 25°C to the reflux temperature of the reaction mixture, very conveniently at the reflux temperature.

The invention also provides a process for the preparation of a compound of formula I wherein X is $N-R^4$ which comprises reacting a compound of formula IV as defined above with a amine of formula R^3R^4NH as defined above.

Reaction of the compound of formula IV with the amine of formula R^3R^4NH may conveniently be effected in the presence of an inert solvent such as those listed above as suitable for reaction of compounds of formula II with compounds of formula III, and at similar temperatures, e.g. at a temperature in the range 25°C to the reflux temperature of the reaction mixture, very conveniently at the reflux temperature.

The compounds of formula II wherein n is O are aminopyridines. Optionally substituted aminopyridines are known materials, or may be prepared by analogous methods to those for preparing known aminopyridines. For example 5-amino-2-chloro-pyridine (3-amino-6-chloropyridine), and 5-amino-2-methoxypyridine (3-amino-6-methoxypyridine) are commercially available, e.g. ex Aldrich Chemie N.V., Brussels, Belgium.

Compounds of formula II wherein n is 1 and R^2 is a hydrogen atom may be prepared by reacting a phthalimide of formula



(V)

wherein R^1 is as defined above with hydrazine, followed by treatment with an acid, conveniently hydrochloric acid. Reaction with hydrazine may conveniently be effected in alcoholic medium, e.g. ethanol, conveniently at reflux temperature.

Compounds of formula V may be prepared by reacting the appropriated halomethyl pyridine, R^1-CH_2-Hal, where R^1 is as defined above and Hal is a halogen atom, preferably chlorine, with an alkali metal phthalimide, e.g. potassium phthalimide.

Reaction may be effected without solvent, and conveniently at a temperature in the range 150 to 170°C, e.g. about 160°C.

Compounds of formula II wherein n is 1 and R^2 is a C_{1-6} alkyl group may be prepared by reacting a C_{1-6} alkylamine with the appropriate halomethyl pyridine R^1-CH_2-Hal, where R^1 is as defined above and Hal is a halogen atom, preferably chlorine. Reaction may conveniently be in alcoholic medium, e.g. ethanol, conveniently at reflux temperature.

Halomethyl pyridines may be prepared by halogenation of the corresponding pyridylcarbinol (hydroxymethyl pyridine). For example, chloromethyl pyridines may conveniently be prepared by reaction of the appropriate pyridylcarbinol with thionylchloride, for example in a haloalkyl solvent such as chloroform, and at reflux temperature.

Some pyridylcarbinols are known, e.g. 3-pyridylcarbinol. In general pyridylcarbinols may be prepared from the appropriate pyridinecarboxylic acid by converision of the acid to the acid chloride followed by reduction of the acid chloride. Optionally substituted pyridinecarboxylic acids are known materials, or may be prepared by analogous methods to those for preparing known pyridinecarboxylic acids. For example, nicotinic acid, 2-chloronicotinic acid, 6-chloronicotinic acid, and 5-bromonicotinic acid are commercially available, e.g. ex Aldrich Chemie N.V., Brussels, Belgium.

The compounds of general formula I exhibit pesticidal, particularly insecticidal, activity. Accordingly the invention also provides a pesticidal composition comprising a carrier and, as active ingredi nt, a compound of general formula I. The invention further provides a method of combating pests at a locus, which comprises treating the locus

with a pesticidal compound or composition according to the invention, and specifically provides the use as an insecticide of a compound of general formula I.

A carrier in a composition according to the invention is any material with which the active ingredient is formulated to facilitate application to the locus to be treated, which may for example be a plant, seed or soil, or to facilitate storage, transport or handling. A carrier may be a solid or a liquid, including a material which is normally gaseous but which has been compressed to form a liquid, and any of the carriers normally used in formulating pesticidal compositions may be used. Preferably compositions according to the invention contain 0.5 to 95% by weight of active ingredient.

Suitable solid carriers include natural and synthetic clays and silicates, for example natural silicas such as diatomaceous earths; magnesium silicates, for example talcs; magnesium aluminium silicates, for example attapulgites and vermiculites; aluminium silicates, for example kaolinites, montmorillonites and micas; calcium carbonate; calcium sulphate; ammonium sulphate; synthetic hydrated silicon oxides and synthetic calcium or aluminium silicates; elements, for example carbon and sulphur; natural and synthetic resins, for example coumarone resins, polyvinyl chloride, and styrene polymers and copolymers; solid polychlorophenols; bitumen; waxes; and solid fertilisers, for example superphosphates.

Suitable liquid carriers include water; alcohols, for example isopropanol and glycols; ketones, for example acetone, methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone; ethers; aromatic or araliphatic hydrocarbons, for example benzene, toluene and xylene; petroleum fractions, for

example kerosine and light mineral oils; chlorinated hydrocarbons, for example carbon tetrachloride, perchloroethylene and trichloroethane. Mixtures of different liquids are often suitable.

Agricultural compositions are often formulated and transported in a concentrated form which is subsequently diluted by the user before application. The presence of small amounts of a carrier which is a surface-active agent facilitates this process of dilution. Thus preferably at least one carrier in a composition according to the invention is a surface-active agent. For example the composition may contain at least two carriers, at least one of which is a surface-active agent.

A surface-active agent may be an emulsifying agent, a dispersing agent or a wetting agent; it may be nonionic or ionic. Examples of suitable surface-active agents include the sodium or calcium salts of polyacrylic acids and lignin sulphonic acids; the condensation products of fatty acids or aliphatic amines or amides containing at least 12 carbon atoms in the molecule with ethylene oxide and/or propylene oxide; fatty acid esters of glycerol, sorbitan, sucrose or pentaerythritol; condensates of these with ethylene oxide and/or propylene oxide; condensation products of fatty alcohol or alkyl phenols for example p-octylphenol or p-octylcresol, with ethylene oxide and/or propylene oxide; sulphates or sulphonates of these condensation products; alkali or alkaline earth metal salts, preferably sodium salts, of sulphuric or sulphonic acid esters containing at least 10 carbon atoms in the molecule, for example sodium lauryl sulphate, sodium secondary alkyl sulphates, sodium salts of sulphonated castor oil, and sodium alkaryl sulphonates such as dodecylbenzene sulphonate; and

polymers of ethylene oxide and copolymers of ethylene oxide and propylene oxide.

The compositions of the invention may for example be formulated as wettable powders, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates and aerosols. Wettable powders usually contain 25, 50 or 75% w of active ingredient and usually contain in addition to solid inert carrier, 3-10% w of a dispersing agent and, where necessary, 0-10% w of stabiliser(s) and/or other additives such as penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and are diluted in the field with further solid carrier to give a composition usually containing ½-10% w of active ingredient. Granules are usually prepared to have a size between 10 and 100 BS mesh (1.676 - 0.152 mm), and may be manufactured by agglomeration or impregnation techniques. Generally, granules will contain ½-75% w active ingredient and 0-10% w of additives such as stabilisers, surfactants, slow release modifiers and binding agents. The so-called "dry flowable powders" consist of relatively small granules having a relatively high concentration of active ingredient. Emulsifiable concentrates usually contian, in addition to a solvent and, when necessary, co-solvent, 10-50% w/v active ingredient, 2-20% w/v emulsifiers and 0-20% w/v of other additives such as stabilisers, penetrants and corrosion inhibitors. Suspension concentrates are usually compounded so as to obtain a stable, non-sedimenting flowable product and usually contain 10-75%w active ingredient, 0.5-15%w of dispersing agents, 0.1-10% w of suspending agents such as protective colloids and thixotropic agents, 0-10% w of other additives such

as defoamers, corrosion inhibitors, stabilisers, penetrants and stickers, and water or an organic liquid in which the active ingredient is substantially insoluble; certain organic solids or inorganic salts may be present dissolved in the formulation to assist in preventing sedimentation or as anti-freeze agents for water.

Aqueous dispersions and emulsion, for example compositions obtained by diluting a wettable powder or a concentrate according to the invention with water, also lie within the scope of the invention. The said emulsions may be of the water-in-oil or of the oil-in-water type, and may have a thick 'mayonnaise'-like consistency.

Compositions in accordance with the invention may also contain other ingredients, for example other compounds possessing pesticidal, herbicidal, or fungicidal properties. The compounds of the invention may be found to be especially useful when applied in admixture with other insecticides and/or acaricides, e.g. organophosphates, pyrethroids, ureas and organotin compounds, for example the commercial products fenvalerate, permethrin, cypermethrin, deltamethrin, alphacypermethrin, fenbutatin oxide, flufenoxuron, diflubenzuron and trefluron.

The invention will be further understood from following illustrative Examples, in which Examples 1 to 6 relate to the preparation of starting materials, Examples 7 to 14 relate to compounds of the invention and their preparation, and Example 15 relates to pesticidal activity tests.

EXAMPLE 1

Preparation of 2-chloro-5-hydroxymethylpyridine

6-Chloronicotinic acid (28.36g, 0.18mol), phosphorus pentachloride (41.65g, 0.20mol) and phosphorus oxychloride (20.50ml, 0.22mol) were

stirred vigorously together at ambient temperature (20°C). The resulting mixture was heated with stirring to 120°C and kept at that temperature for a further 3 hours. The mixture was then allowed to cool to ambient temperature (20°C) and excess phosphorus oxychloride was evaporated off under reduced pressure to yield 6-chloronicotinyl chloride as a brown oil (31.68g, 100%), which was used directly in the following step.

Sodium borohydride (24.97g, 0.66 mol) and ice/water (400ml) were stirred with ice/salt bath cooling. The 6-chloronicotinyl chloride (31.68g, 0.18mol) was added to the resulting mixture to ensure that, with ice/salt bath cooling, the temperature of the mixture did not rise above 15°C. After addition was complete the temperature of the mixture was allowed to rise to ambient temperature (20°C) and was stirred at this temperature for 12 hours. The mixture was then extracted with dichloromethane (8 x 200ml). The combined extracts were dried (Mg SO_4) and evaporated under reduced pressure to give a white solid. The title product, 2-chloro-5-hydroxymethyl-pyridine, was isolated from this white solid by flash chromatography using silica gel, 230 to 400 US mesh (0.062mm to 0.037mm), with diethylether as eluent, as a white solid (18.76g, 72.6%).

NMR ($CDCl_3$), delta (ppm): 3.70 (broad, 1H), 4.66(s,2H), 7.27 (d,1H), 7.65 (d/d, 1H), 8.25(s,1H).

EXAMPLE 2

Preparation of 2-chloro-5-chloromethylpyridine

Thionyl chloride (14.6ml, 0.2mol) was added extremely carefully in dropwise manner to a rapidly stirred mixture of 2-chloro-5-hydroxymethylpyridine (18,6g, 0.13mol) and chloroform (150ml) at ambient temperature (20°C). After addition was complete the

resulting mixture was heated under reflux for 12 hours. The reaction mixture was then allowed to cool to ambient temperature (20°C) and chloroform was evaporated off under reduced pressure to give a brown oil. The title product, 2-chloro-5-chloromethyl-pyridine was isolated from this brown oil by flash chromatography using silica gel, 230 to 400 US mesh (0.062mm to 0.037mm), with dichloromethane as eluent, as a brown oil which solidified on standing (17.45g, 82.9%).

NMR ($CDCl_3$), delta (ppm): 4.51(s,2H), 7.28(d,1H), 7.65 (d/d,1H), 8.32(d,1H).

EXAMPLE 3

Preparation of N-(6-chloro-3-pyridylmethyl) phthalimide

2-Chloro-5-chloromethylpyridine (8.1g, 0.05mol) and potassium phthalimide (10.2g, 0.055 mol) were mixed together at ambient temperature (20°C) and the resulting mixture was then heated with stirring at 160°C for 12 hours. The reaction mixture was then cooled to ambient temperature (20°C) and dichloromethane was added until most of the solid residue had dissolved. The dichloromethane extract was then washed with water (2 x 150ml) and brine (1 x 200ml), dried ($MgSO_4$), and evaporated under reduced pressure to give a light-brown solid. The title product, N-(6-chloro-3-pyridylmethyl) phthalimide, was isolated from this solid by flash chromatography using silica gel, 230 to 400 US mesh (0.062mm to 0.037mm), with 10% v/v ether/dichloromethane as eluent, as a buff solid (10.70g, 78.5%), mp 140 to 142°C.

NMR ($CDCl_3$), delta (ppm): 4.81 (s,2H), 7.25 (d,1H), 7.72 (m,3H), 7.83 (m,2H), 8.47 (d,1H).

EXAMPLE 4

Preparation of 5-aminomethyl-2-chloropyridine

Hydrazine hydrate (2.00ml, 0.04mol) was added at ambient temperature (20°C) to a solution of N-(6-chloro-3-pyridylmethyl) phthalimide (10.70g, 0.039mol) in ethanol (150ml), and the resulting solution was heated under reflux for 4 hours before being cooled to ambient temperature (20°C). 25% w/v Aqueous hydrochloric acid (60ml) was added directly and the resulting mixture was heated under reflux for 1 hour. The reaction mixture was then cooled to ambient temperature (20°C), filtered and evaporated under reduced pressure. The resulting concentrated mixture was filtered and the filtrate was cooled, with ice/salt bath cooling, and solid potassium hydroxide was added with stirring until the mixture became basic. The reaction mixture was then extracted with diethylether (5 x 150ml). The combined ether extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the title product, 5-aminomethyl-2-chloropyridine as a brown oil (5.07g, 90.6%).

NMR($CDCl_3$), delta (ppm): 1.48 (broad, 2H), 3.81 (s,2H), 7.21 (d,1H), 7.59 (d/d,1H), 8.24(s,1H).

EXAMPLE 5

Preparation of 2-chloro-5-methylaminomethylpyridine

A mixture of 2-chloro-5-chloromethylpyridine (8.1g, 0.05mol), methylamine (60ml of a 30% w/v solution in water, 0.5mol) and ethanol (100ml) was heated, with stirring, under reflux for 5 hours. The reaction mixture was then cooled to ambient temperature (20°C) and evaporated under reduced pressure to give a brown oil. The title product, 2-chloro-5-methylaminomethylpyridine, was isolated

from this oil by flash chromatography using silica gel, 230 to 400 US mesh (0.062mm to 0.037mm), with 10% v/v methanol/dichloromethane as eluent, as a brown oil (5.96g, 76.1%).

NMR ($CDCl_3$), delta (ppm): 1.66 (broad s,1H), 2.37 (s,3H), 3.67 (s,2H), 7.21 (d,1H), 7.59 (d/d, 1H), 8.24 (s,1H).

EXAMPLE 6

By a process analogous to that of Example 5, 2-chloro-5-ethylaminomethylpyridine was prepared, as a brown oil (81.8%).

NMR ($CDCl_3$), delta (ppm): 1.05(t,3H), 1.56 (s,1H), 2.59(quart.,2H), 3.71(s,2H), 7.20(d,1H), 7.60(d/d,1H), 8.23(s,1H).

EXAMPLE 7

Preparation of 1-(6-chloro-3-pyridylmethylamino)-1-methylthio-2-nitroethene

A solution of 5-aminomethyl-2-chloropyridine (1.78g, 0.0125 mol) in ethanol (15ml) was added dropwise to a mixture of 1,1-bis (methylthio)-2-nitroethene (4.13g, 0.025 mol) and ethanol (50ml) at reflux temperature. When addition was complete, the resulting mixture was heated under reflux for 3 hours, after which it was cooled to ambient temperature (20°C) and evaporated under reduced pressure to give a yellow solid. The title product, 1-(6-chloro-3-pyridylmethylamino)-1-methylthio-2-nitroethene, was isolated from this solid by flash chromatography using silica gel, 230 to 400 US mesh (0.062mm to 0.037mm), with 10% v/v ether/dichloromethane as eluent, followed by recrystallisation from ethanol as a brown solid (2.61g, 80.4%), mp 157 to 160°C.

NMR($CDCl_3$), delta (ppm): 2.44(s,3H), 4.65 (d,2H), 6.58 (s,1H), 7.35 (d,1H), 7.63 (d/d,1H), 8.35(d,1H), 10.70 (broad,1H).

EXAMPLE 8

Preparation of 1-(6-chloro-3-pyridylmethylamino)-1-methylamino-2-nitroethene

A mixture of 1-(6-chloro-3-pyridylmethylamino)-1-methylthio-2-nitroethene (2.60g, 0.01mol), methylamine (1.90g of a 33% w/w/ solution in ethanol, 0.02mol) and ethanol (50ml) was heated, with stirring, under reflux for 1 hour. The reaction mixture was then cooled to ambient temperature (20°C) and evaporated under reduced pressure to give a light brown solid, which was recrystallised from ethanol to give the title product, 1-(6-chloro-3-pyridylmethylamino)-1-methylamino-2-nitroethene, as a light brown solid (1.32g, 54.3%), mp 181 to 183°C.

NMR (D_6 dimethylsulphoxide), delta (ppm): 2.89 (broad,3H), 4.38 (broad,2H), 6.40 (broad,1H), 7.49 (d,1H), 7.67 (broad, 1H), 7.85 (d,1H), 8.35 (s,1H).

EXAMPLES 9 TO 14

Using the appropriate pyridine derivatives of Examples 4 to 6, or, in the case of Example 14, 2-chloro-5-aminopyridine, the following additional compounds were prepared by similar processes to those of Examples 7 and 8:-

9: 1-[N-methyl-N-(6-chloro-3-pyridylmethyl)amino]-1-methylamino-2-nitroethene (68.8%), mp 102 to 104°C.

NMR ($CDCl_3$),delta (ppm): 2.77(s,3H), 3.03(d,3H), 4.36(s,2H), 6.45(s,1H), 7.32(d,1H), 7.53(d/d, 1H) 8.25(s,1H) 9.67(broad,1H).

10: 1-[N-ethyl-N-(6-chloro-3-pyridylmethyl)amino]-1-methylamino-2-nitroethene (82.7%), yellow gum.
NMR ($CDCl_3$), delta(ppm): 1.17(t,3H), 3.05(d,3H), 3.12(quart.,2H), 4.33 (s,2H), 6.51(s,1H), 7.34(d,1H), 7.53(d,1H), 9.81(broad,1H).

11: 1-[N-ethyl-N-(6-chloro-3-pyridylmethyl)amino]-1-dimethylamino-2-nitroethene (78.9%), yellow gum.
NMR ($CDCl_3$), delta(ppm): 1.11(t,3H), 2.88(s,6H), 3.06(quart.,2H), 4.33(s,2H), 6.30(s,1H), 7.26(d,1H), 7.59(d,1H), 8.22(s,1H).

12: 1-(6-chloro-3-pyridylmethylamino)-1-dimethylamino-2-nitroethene (51.7%),mp 122 to 124°C.
NMR ($CDCl_3$), delta(ppm): 2.92(s,6H), 4.45(d,2H), 6.49(s,1H), 7.33(d,1H), 7.67(d/d,1H), 8.32(d,1H), 9.69 (broad,1H).

13: 1-(6-chloro-3-pyridylmethylamino)-1-ethylamino-2-nitroethene (55.3%), mp 182 to 184°C.
NMR ($CDCl_3$), delta(ppm): 1.09(broad,3H), 3.25 (broad,2H), 4.38 (broad,2H), 6.40 (broad,1H), 7.49(d,1H), 7.55(d/d,1H), 7.55 (broad,1H), 8.35(s,1H), 9.96(broad,1H).

14: 1-(6-chloro-3-pyridylamino)-1-methylamino-2-nitroethene (65.9%), mp 175-177°C (decomposition).

NMR (D_6 dimethylsulphoxide), delta (ppm):
2.89(broad,3H), 6.15(broad,1H),
7.54(d,1H), 7.75(d/d,1H),
8.29(d,1H), 8.5-10.3(broad,2H).

EXAMPLE 15

Pesticidal Activity

Pesticidal activity of compounds of the invention was assessed against various of the following pests:-

Spodoptera littoralis (Egyptian cotton leafworm)
Aedes aegypti (yellow fever mosquito)
Musca domestica (housefly)
Acyrthosiphon pisum (pea aphid)
Nephotettix cincticeps (green leaf hopper)
Nilaparvata lugens (brown rice plant hopper)

The test methods employed for each species appear below. In each test, unless otherwise stated, solutions or suspensions of test compound were made up over a range of concentrations in water (initially 0.1%w) contianing 10%w acetone and 0.025%w "TRITON X-100" (trade mark) surface active agent (the condensation product of ethylene oxide with an alkyl phenol). These solutions were sprayed at a rate equivalent to 340 litres per hectare ($3.4 \times 10^{-5} m^3/m^2$) onto Petri dishes containing either test species per se or diet onto which test species were subsequently introduced, as indicated. The tests were all conducted under normal insectary conditions ($23^{\circ}C \pm 2^{\circ}C$, fluctuating humidity and light).

The results of testing at the initial test concentrations were graded A, B or C.

Grade A represents at least 70% mortality of the pest,

Grade B represents between 40% and 70% mortality, and

Grade C represents less than 40% mortality.

For compounds achieving Grade A at initial test concentration, mortality assessments were made as indicated below, in terms of percentage mortality figures. In each test a LC_{50} (the dosage of active material required to kill half of the test species) for the compound was claculated from the mortality figures and compared with the corresponding LC_{50} for a standard insecticide, ethyl parathion, in the same test. The results are expressed as toxicity indices thus:

$$\text{toxicity index} = \frac{LC_{50} \text{ (parathion)}}{LC_{50} \text{ (test compound)}} \times 100$$

(i) Spodoptera littoralis (7 day) (Sl 7D)

Test solutions were sprayed as indicated above onto Petri dishes containing a nutritious diet for Egyptian cotton leafworm larvae. When the spray deposit had dried, each dish was infested with ten 2nd instar larvae. morality assessments were made 7 days after spraying.

(ii) Spodoptera littoralis (foliar) (Sl Fol)

Test solutions were sprayed as described above onto Petri dishes containing 9cm discs of Chinese cabbage leaves on filter papers. After drying, each dish was infested with ten 2nd instar larvae. Mortality assessments were made 24 hours after infestation.

(iii) Spodoptera littoralis (ovicidal) (Sl OA)

Test solutions were sprayed as described above onto Petri dishes containing filter papers on which were 50 24 hours old ggs. After 6 days the numbers

of hatched and unhatched eggs were counted and percentage morality calculated.

(iv) Aedes aegypti (Aa)

Early 4th instar larvae were used. Test solutions were made up to 0.5 ppm of test compound (and progressive half-dilutions) in water containing 0.04%w "TRITON X-100" (trade mark); acetone was initially present to aid solution, but was allowed to evaporate off before introduction of larvae.

Ten early 4th instar larvae were placed in 100 ml of test solution, and after 48 hours, larval mortality was recorded.

(v) Musca domestica (Md)

Batches of ten 2 to 3 day old milk-fed adult female houseflies, anaesthetised using carbon dioxide, were placed on filter papers inside Petri dishes. The dishes were sprayed with the test solutions as described above. The flies were retained in the Petri dishes and were fed with a dilute milk solution whcih was dripped down the side of the Petri dish and absorbed by the filter paper. Mortality was assessed after 24 hours.

(vi) Acyrthosiphon pisum (Ap)

Tests were carried out on young adult pea aphids. Whole pea plants 6 days after germination were placed on filter papers in Petri dishes. Ten aphids were trnasferred to each pea plant and left for 30 minutes to allow the aphids to settle and start to feed. The dishes were then sprayed with the test solutions as described above and lids were placed on the Petri dishes. Mortality was assessed after 24 hours.

(vii) Nephotettix cincticeps (Nc)

Tests were carried out on young adult female green leaf hoppers. Plant pots, each containing five rice seedlings 10 to 15 cm tall arranged across the

centre of the pot, were sprayed with test solutions as described above (but initial test concentration 0.05% of test compound). Spraying was on both sides of the plants with the pots horizontal. One hour after spraying, each pot was filled to the brim with fine silver sand, an open-ended glass jar was placed over each pot and each pot was infested with ten hoppers. A paper tissue was placed over the open end of each glass jar to retain the hoppers. The pots were irrigated from underneath, maintained at a temperature of 27°C ± 2°C and subjected to white fluorescent light under a regime of 18 hours light followed by 6 hours darkness. Mortality assessments were made 48 hours after infestation.

(viii) Nilaparvata lugens (N1)

Tests were carried out on young adult female brown rice plant hoppers in the same way as for green leaf hoppers in (vii) above.

Results of the above tests, only some of which were performed on each compound, are given in Table I following:

TABLE I

Compound of Example	Toxicity Indices							
	S1 7D	S1 Fol	S1 OA	Aa	Md	Ap	Nc	N1
7	7		18	A	A	8	24	<20
8	5	280		3	1	130	2482	
9	B	A		A	1	A	10350	
10				A	1	93	36500	
11				A	3		14270	
12				1			466	3100
13							42	
14		A	20	A	2	3	507	
Comparative A	C		C	C	C	C	C	

"Comparative A" is the compound 1-(6-chloro-3-pyridylmethylamino)-1-n-propylamino-2-nitroethene, mp 169 to 172°C, which was prepared in analogous manner to Example 8.

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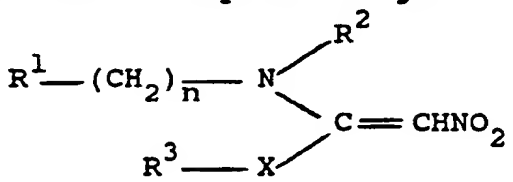
CLAIMS

1. A nitroethene compound of general formula



(I)

wherein n is 0 or 1, X represents a sulphur atom or a group N-R^4, R^1 represents an optionally substituted pyridyl group, R^2 represents a hydrogen atom or a C_{1-6} alkyl group, R^3 represents a methyl or ethyl group and R^4 represents a hydrogen atom or a methyl or ethyl group.

2. A compound according to Claim 1 wherein R^1 is an optionally substituted 3-pyridyl group.

3. A compound according to Claim 1 or 2 wherein R^1 is a 3-pyridyl group subsituted in the 6-position by a halogen atom, a C_{1-4} alkoxy group, a C_{1-4} alkylthio group, a C_{1-4} haloalkyl group, a cyano group or a (C_{1-4} alkoxy) carbonyl group.

4. A compound according to Claim 1, 2 or 3 wherein R^1 is a 3-pyridyl group substituted in the 6-position by a chlorine or bromine atom, a methoxy group, a di- or trifluoromethyl group, or a cyano group.

5. A compound according to any one of Claims 1 to 4 wherein R^1 is a 6-chloro-3-pyridyl group.

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6. A compound according to any one of Claims 1 to 5 wherein R^2 is a hydrogen atom or a C_{1-4} alkyl group.

7. A compound according to any one of Claims 1 to 6 wherein R^2 is a hydrogen atom or a methyl or ethyl group.

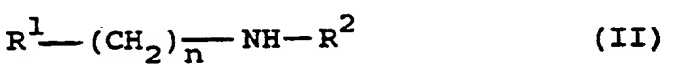
8. A compound according to any one of Claims 1 to 7 wherein X is $N-R^4$.

9. A compound according to Claim 8 wherein R^3 is a methyl group and R^4 is a hydrogen atom or a methyl group.

10. A compound according to any one of Claims 1 to 9 wherein n is 1.

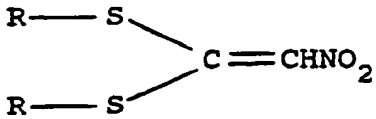
11. A compound according to Claim 1 as described in any one of Examples 7 to 14.

12. A process for the preparation of a compound of general formula I as defined in any one of Claims 1 to 10 which comprises reacting a compound of formula



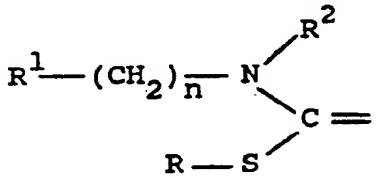
(II)

wherein n, R^1 and R^2 are as defined in Claim 1 with a nitroethene compound of formula



(III)

wherein R represents a C_{1-4} alkyl group, to produce a nitroethene compound of formula



(IV)

followed, optionally wh re R is R^3, by reacting the compound of formula IV with an amine of formula R^2R^4NH wherein R^3 and R^4 are as defined

in Claim 1, to produce a compound of formula I wherein X is $N-R^4$.

13. A process for the preparation of a compound of formula I as defined in Claim 8 which comprises reacting a compound of formula IV as defined in Claim 12 with an amine of formula R^3R^4NH as defined in Claim 12.

14. A process according to Claim 12 substantially as hereinbefore described with reference to any one of Examples 7 to 14.

15. A process according to Claim 13 substantially as hereinbefore described with reference to any one of Examples 8 to 14.

16. A pesticidal composition comprising a carrier and, as active ingredient, a compound according to any one of Claims 1 to 11.

17. A method of combating pests at a locus which comprises treating the locus with a compound of formula I as defined in any one of Claims 1 to 11.

18. The use as an insecticide of a compound of formula I as defined in any one of Claims 1 to 11.

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